Characteristics of extra polymer layer doped with ($BaTiO_3$) nanoparticles: polymer dispersed liquid crystal display

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In this article, we proposed a new technique for the improvement of contrast ratio (CR) of the ($BaTiO_3$) nanoparticle doped polymer dispersed liquid crystals (Np-PDLC) display. For the purpose, an extra polymer layer has been employed at the lowermost part of the nanoparticle doped-PDLC film. By adopting such technique, we found significantly improved electro-optical contrast of Np-PDLC film. The contrast ratio of the Np-doped PDLC device fabricated with extra polymer layer (PDLC-C) offered 7.24, which was found as the best among all the fabricated devices. The results of the study have been verified by experimental techniques. Such technique has been found easy to employ and could be used for attaining better Np-PDLC display. All the results have been discussed in detail. The current Np-doped PDLC methodology could be useful for various display applications.

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1. Introduction

Polymer dispersed liquid crystal (PDLC) displays due to their advantageous features have gained much attention among the various display groups [1-3]. Some of the useful aspects of such PDLC-based applications include electro-optical devices and information displays device manufacturing. PDLC films provide low cost production, simple fabrication process and improved applicability in the large area scale in display devices which make them exceptional over the conventional LC display [3].

Considering the importance of this display technology, an intensive amount of work has been performed for the improvement of electro-optical response of PDLC display devices. Many groups are working for the further development of the PDLC films, which suggest introducing new dye doping materials into the PDLC mixture [4-6], while other suggest the insertion of nanoparticles (Np) into the PDLC films [7-8]. However, the addition of Np materials resulted into the higher scattering into the PDLC films, while the insertion of dye reduces to nominal contrast ratio (CR) of the PDLC film. In particular, the Np-doped PDLC films exhibit better performance as compared to simple PDLC materials due to their improved contrast ratio (CR) and time response [7-8].

Recently nanoparticles (Np) have attracted great interest due to their exceptional mechanical, optical and magnetic properties [7-8]. Additional advantages of Np-doped PDLC films give better electro-optical contrast and such Np-doped devices create a strong network in LC layers, which prevent pouring effects in the cells [9-10]. However, the improvement in the electro-optical properties of PDLCs is associated with the size, type, concentration and intrinsic characteristics of the nanoparticles [11]. It is suggested to use the nanoparticles that have comparable properties with LC molecules and of an optimum size that should not disrupt the order of the LC. Hence, low concentrations of Nps are usually preferred to yield a more stable and evenly distribution in the PDLCs [12].

Nevertheless, even on today, owing to the useful features of Np-doped materials such nanoparticles are not often employed into LC industry due to their negative impact equally distribution of nanopaticles, leading to irregular size distribution of LC droplets and restriction to use the minimal amount of such materials. The present work is an attempt to overcome such weakness of Np-PDLCs and to develop a nanoparticle doped PDLC owning good electro-optical properties. In order to, explore the effect of fabrication procedures on the electro-optical properties of Nps doped PDLCs, diverse methods are adopted. This is done to cut off the drawback of quantity of nanoparticles used inside PDLCs and to get the better performance of Np based PDLCs. For the purpose in this work, we have used $BaTiO_3$ polyhedron-shaped ferroelectric nanoparticle with PN393 monomer and E7 liquid crystal. The following devices have been studied in detail using the various analysis techniques.

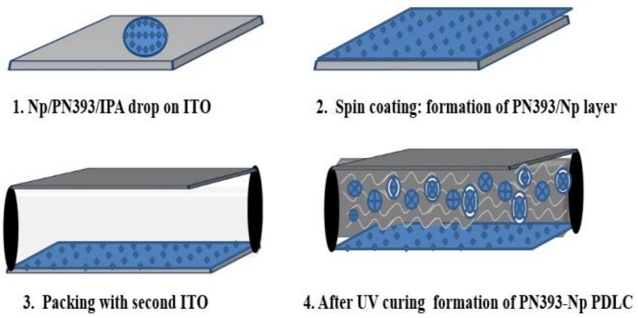

Fig. 1. Step by step schematic procedure for the fabrication of the PDLC-C device

2. Experimental

2.1. Materials and methods

The PDLC composition was a mixture of nematic liquid crystal E7 (Merck, n_o = 1.5217, $\Delta\varepsilon$ = +13.8) which was a eutectic mixture of three Liquid crystals of cyanobiphenyls and a cyanoterphenyl. A commercial monomer mixture PN393 (Merck, n_p = 1.499) was used. The two materials were mixed with 79:21 weight ratios. The Titanium barium oxide **(**$BaTiO_3$, Sigma-Aldrich) was used as nanoparticle (Np). These nanoparticles are the ferroelectric particles type. Previously they are used to improve the spontaneous polarization and the electro-optical properties and response time of the LC devices. Also, such utilization of ferroelectric nanoparticles improves the response time [12]. The size of nanoparticle was < 100 nm. The nanoparticles were used with 1.8 wt%. To define the gap of the conventional PDLC cell, mylor spacers of 20 μm diameters size have been used. Indium–tin–oxide (ITO) coated glass is used as the device substrate.

2.2. PDLC fabrication

To get the optimum electro-optical (EO) contrast the various fabrications procedures are adopted for nanoparticles PDLC films. The details procedure employed for the fabrication of proposed PDLC film has been shown in Fig. 1.

According to this technique in the first step, three PDLCs A, B, C are fabricated. The PDLC-A is fabricated with mixture of E7, PN393 of 79:21 wt% and BaTiO3 Np with 1.8 wt%. The PDLC-B device has two layers. One layer is fabricated with E7, PN393 of 79:21 wt% and BaTiO3 Np with 1.8 wt%. The other layer of device has been developed by mixture of PN393/isopropyl alcohol (IPA). The PN393 is mixed in IPA with 1:1.5 wt%. The PN393/IPA mixture is coated on ITO glass with spin coating technique. For the device PDLC-C, initially Np/PN393/IPA layer is made up by spin coating technique on ITO glass by using the PN393 mixture with IPA of 1:1.5 wt% and nanoparticles with 1.8 wt%. Next to this, a PDLC-C is fabricated by dropping and curing the E7 and PN393 (79:21 wt%) mixture on the initially coated ITO glass.

The curing conditions for the devices are kept fixed at room temperature, 10 minutes of curing. The UV light used for curing the monomers has 360 nm of wavelength of 20 mJ/cm^2 intensity.

3. Results and discussion

Generally, by dispersing the nanoparticles inside PDLCs the electro-optical properties are enhanced, such as contrast ratios and fast switching time by decreasing the inter molecular forces [13]. However, the enhanced electro-optical properties of nanoparticles doped PDLCs are strongly dependent on nanoparticles size and contents. A little exceed in Nps contents a deterioration in electro-optical properties are observed. To cutback such flaws, the nanoparticles doped PDLCs at higher percentage are made by varying fabricating procedures. The three PDLCs are named as PDLC-A, PDLC-B and PDLC-C by adoptive procedures. The detailed process for fabrication of PDLC-A, PDLC-B, and PDLC-C is described in experimental section and shown in Fig. 1.

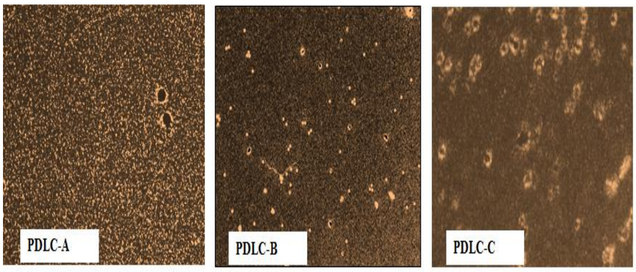

Fig. 2. The morphologies of PDLC-A, PDLC-B and PDLC-C devices as observed under the microscope

3.1. PDLC morphology

Once the fabrication has been performed, the characteristics of these device have been studied in detail. The droplet/domain size of PDLC films are controlled by many factors, some of important factors are e.g., the rate of polymerization, rate of phase separation and interactions of PDLC material with the ITO glass [14-17].

At first, the morphologies of these devices have been studied by polarized optical microscope using 4X magnification lens. Various amount distributions for nanoparticles have been observed by applying the three different techniques, which can be seen in Fig. 2 and 3. Fig. 2 displayed the morphologies of nanoparticles based PDLCs devices after curing. By microscopic surface view it was supposed that by insertion of nanoparticles at higher amount no noticeable alteration in PDLC morphologies and droplet size was observed. The similar effect has been viewed by others as well [9-10].

To understand the clear changes in PDLC droplet morphologies these devices have been dipped into isopropyl alcohol and acetone mixture for about 15 days, then LC molecules are excluded. Further, these were dried in vacuum and observed again under the microscope. This gave the detailed analysis about change in morphology and shown in Fig. 3. The morphology of PDLC-A showed small sized LCs droplets less than 20 µm. PDLC-A is fabricated by doping the 1.8 wt% of $BaTiO_3$ Np inside PDLC. Generally, LC droplets sizes found before was of 5-20 µm in sizes [9-10]. Our findings showed the regular in size distribution for LC droplets. PDLC-B showed the formation of comparatively small sized LC droplets. PDLC-B is formed by the building an extra layer of PN393 under the Nps doped PDLC device. It seems the droplet size decreased for the PDLC-B. It was perhaps disruption in attracting forces among PDLC film and ITO glass. Next to this, Fig. 3 showed the morphology of PDLC-C device. PDLC-C is fabricated by constructing an extra layer of Np/PN393/IPA layer under the E7/PN393 PDLC. The 1.8 wt% of Nps percentage were used in mixture of PN393/IPA to construct the extra layer. The Fig. 3 showed the interesting image for Nps doped in PN393 layer over the PDLC. This clearly displayed that tinny nano partilces are enwrapped in the polymer domains with the dispersion on the PDLC device. These domains are clearly shown smaller in size than 20 µm, although lager in size from PDLC devices A & B. This indicated that the groups of Nps trapped in the polymer matrix spherical regular stack. Such controlled microstructure formation of Nps are supposed to be due to use of isopropyl alcohol as solvent in the PN393/Np medium. Previously some studies have showed the effect of medium on the micro structure of $BaTiO_3$ [18]. All such findings proving that Nps doping by three different ways has obvious effect on the electro-optical properties of PDLC devices. The electro-optical properties of the following devices are observed further with voltage and are displayed in Fig. 4 and 5.

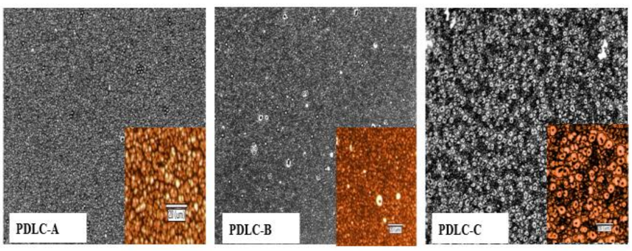

Fig. 3. The morphologies of PDLC-A, PDLC-B and PDLC-C devices as observed under the microscope after washing out of LCs

3.2. Electro-optical properties

Once the morphology of PDLC devices is observed the electro-optical characteristics of these device has been studied in detail. To observe any change in electro-optical properties the transmittance with voltage and contrast ratio is observed. These properties are displayed in Fig. 4, 5 respectively**.** Particularly in Fig. 4 a regular size distribution of nano particles is observed by adopting the new procedure, which is quite useful and innovative effect of this new technique.

Fig. 4 showed the electro-optical response of transmittance with voltage of PDLC devices. It is observed that Off transmittance (T_{Off}) for three devices showed obvious change in characteristics due to insertion of Nps, PN393 layer or Np-PN393 layer. The PDLC-A exhibited T_{Off} at 16 percentages. As the PN393 layer is introduced under the Np-PDLC a decrease in T_{Off} is observed at 12.05% for PDLC-B. However, on fabricating of extra polymer layer dispersed with Nps a clear decrease in the To_{ff} is observed (9.8%) for PDLC-C. This decrease in T_{Off} is possible due to the formation of extra polymer layer as well as the dispersion of tinny nanoparticles that may enhanced the extra scattering while there is no applied voltage. Previously an effect of Nps doped inside PDLC is observed on the controlling voltages and contrast ratios [9-10]. The change was suggested as by modification of dielectric permittivity of the polymer phase which may decrease the effective electric field applied to the devices. Further, it is proposed that doping of with inorganic Np may improve the thermal and mechanical stability of the polymer matrix. Additionally, a little inflection in transmittance (T_{On}) at 50 applied voltage is observed. These findings are mentioned in Table 1.

The contrast ratios of the following devices are observed with the applied voltages and plotted in Fig. 5. The device PDLC-A showed the maximum contrast at 4.5 and PDLC-B showed an increase in CR as 5.47. However, obvious increase in CR is observed for the PDLC-C device that showed maximum CR as 7.24. The increase in CR for PDLC-B is possibly due to extra polymer layer while for the PDLC-C this behavior is possible due to multiple scattering of Np/PN393 extra layer and that may have lessen the intermolecular interactions among the ITO glass and LC droplets of PDLC film. Following findings are mentioned in the Table 1.

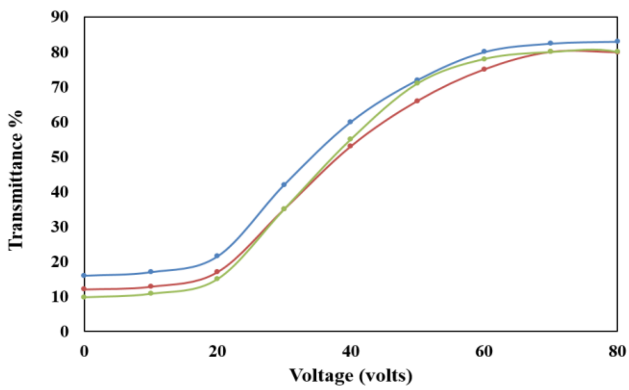

Fig. 4. A view of the transmittance Vs Voltage response of three prepared PDLC devices

Afterwards from the transmittance vs volt findings the threshold voltage (V_{th}) and saturation voltage (V_{sat}) are observed and plotted in Table 1. The threshold voltage (V_{th}) is the minimum volt required to show the 10% of transmittance. The saturation volt is the volt where PDLC showed its maximum transmittance properties. Such finding is tabulated in Table 1. It is obvious from the table that the PDLC-A devices fabricated with Np doped PDLC mixture showed V_{th} and V_{sat} voltages as 18.5 and 46 respectively values. Further, for the PDLC-B it showed V_{th} and V_{sat} 19 and 46 respectively. This showed a less effect of formation of extra layer on the V_{sat} and V_{th} voltages. Further for the PDLC-C the V_{sat}, V_{th} has been found as 19.2 and 48, respectively. This showed a little increase in V_{sat}. However collectively it showed a less effect on the V_{th} and V_{sat}.

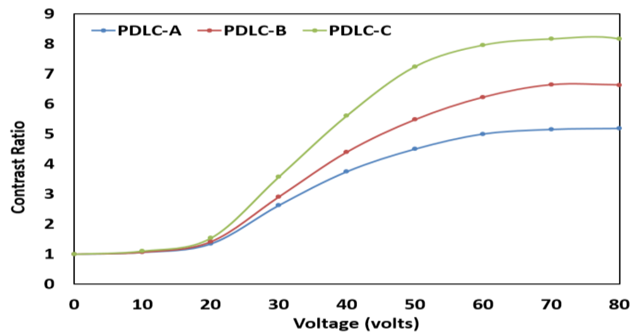

Fig. 5. A view of the contrast ratio (CR) Vs Voltage response of three prepared PDLC devices

Table 1. The electro- optical properties of PDLC devices

	T_{Off}	T_{On}	CR	V_{th}	V_{sat}
PDLC-A	16	72	4.5	18.5	46
PDLC-B	12.05	66	5.47	19	46
PDLC-C	9.8	71	7.24	19.2	48

4. Conclusions

In this work, we proposed a new technique for the improvement of the electro-optical contrast of Np based PDLCs film by inserting additional polymer or Np-polymer layer. Our experimental findings indicated that the front location of Np-doped polymer layer could improve the CR by decreasing the T_{Off} due to increase in multi-directional scattering properties of PDLC device. This behavior is considered as due to the decrease in surface interfacial interactions properties by inserting the nanoparticles on the ITO glass using with PN393 layer. This study can be a useful addition in the nanoparticles doped PDLC devices for their many display applications.

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